

ANNUAL REPORT

TO **NASA CR 70970**

NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION

ON

EFFECT OF WATER PROPERTIES  
IN THIXOTROPIC CLAY SYSTEMS  
ON BIOLOGICAL ACTIVITY

(Contract No. NGR 15-007-004)

Submitted by

Dr. Philip F. Low  
Department of Agronomy  
Purdue University  
West Lafayette, Indiana

FACILITY FORM 602

**N67-17767**  
(ACCESSION NUMBER)

**CR 70970**  
(PAGES)  
(NASA CR OR TMX OR AD NUMBER)

(THRU)  
(CODE) **04**  
(CATEGORY)


GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 3.00

Microfiche (MF) .65

This project was activated on January 1, 1965. However, Dr. Brian G. Davey, the Post-Doctoral Research Associate assigned to it, did not arrive until the end of January. The Calvet microcalorimeter, which was essential to the project, was not received from France until about April. Between the time of his arrival and the receipt of the microcalorimeter, Dr. Davey became acquainted with the literature related to the problem and prepared a large quantity of Na-saturated, Wyoming bentonite (clay). When the microcalorimeter arrived he began immediately to install it. However, it was found that the rooms reserved for the microcalorimeter had to be remodelled extensively before it could be put into operation. The remodeling consumed considerable time. Then it was found that building vibrations prevented the satisfactory operation of the recording equipment that accompanied the instrument. Consequently, recording equipment of a different type was ordered. When the latter equipment was put in operation, difficulty was encountered with ground loops and shielding. After this difficulty was overcome, it was found that one of the thermopiles in the microcalorimeter had been damaged slightly in transit and produced too much electrical noise. Therefore, new matched thermopiles (a differential technique is employed) were requested from the manufacturer. Customs clearance in New York delayed their arrival. And it was necessary to disassemble the microcalorimeter entirely to install them. The net result was that the microcalorimeter, which was indispensable to the program, was not operating successfully until the end of September. Thereafter, it had to be accurately calibrated and experience had to be gained relative to its use. Since Dr. Davey had to



leave in January, 1966, too little time was left for him to perform more than preliminary experiments with it. However, the preliminary experiments gave exciting results. They, and other experiments not involving the microcalorimeter, are reported hereafter.

During the measurement of the relative partial molar free energy of water in clay sols and gels with an osmometer, it became apparent that the magnitude of the osmotic pressure of these systems was dependent on the size of the pores in the membrane. This led to an examination of different membranes and the construction of a new miniature osmometer that employs a transducer to measure the osmotic pressure and a potentiometric recorder to record it. With this instrument osmotic pressures of colloidal suspensions can be measured to less than a cm. of water in a few hours. And less than 0.5 ml. of suspension is required. It is anticipated that this osmometer will have extensive use in future work in this and other laboratories.

To determine the minimum clay concentration at which gelation occurs in a clay-water suspension, a Fann viscosimeter was used. The results showed that essentially no torque was exerted on the viscosimeter bob, when the surrounding suspension was set in motion by the rotor, until the suspension contained 4 percent clay by weight. Then the torque increased rapidly with clay concentration. Hence, the minimum concentration of clay required for gelation was assumed to be 4 percent.

The NaCl activity was measured in suspensions containing  $10^{-4}$  N NaCl and different concentrations of clay. This activity was measured with a

Ag-AgCl electrode and a sodium-ion electrode couple. When the NaCl activity was plotted against the clay concentration, two straight lines having different slopes were produced. The intersection of these lines was at 4 percent clay by weight. Therefore, it is evident that gelation changes the NaCl activity. It is postulated that this change in activity is the result of the change in water properties that accompanies gelation.

Gel strengths of clay pastes having different prior mechanical treatments were also determined in the viscosimeter. It was found that pastes injected into the viscosimeter from an 18-gauge hypodermic needle had greater gel strength than those remolded and introduced with a spatula. Spinning the pastes between the rotor and bob reduced the gel strength but jarring them subsequently increased it again. The gel strength was increased by allowing the system to stand undisturbed when the space between the rotor and bob was large. However, very little increase in gel strength occurred when this space was small. The viscosimeter study illustrates the fact that the state of a clay-water system depends on its history. This fact must be taken into account in all future studies.

When heats of gelation were determined in the microcalorimeter on these same pastes, it was found that those injected into the calorimetric cell from the 18-gauge needle had essentially no heat of gelation. The same was true of those pastes that had been jarred vigorously. Evidently these pastes were in their equilibrium states. Since the needle injection would have oriented the flat clay particles in a parallel array, it may be

assumed that one equilibrium state has this kind of particle arrangement. Evidently, this state has relatively great shear strength. Those pastes that were remolded and introduced into the calorimetric cell with a spatula, or that were stirred in the cell, exhibited heats of gelation. Heat was given out on gelation at  $25^{\circ}\text{C}$ ; it was taken in at  $30^{\circ}\text{C}$ . It is believed that the heat given out at  $25^{\circ}\text{C}$ . represents the true heat of gelation. However, the heat taken in at  $30^{\circ}\text{C}$ . is not likely due to gelation per se because it is contrary to the first law of thermodynamics for a system to spontaneously increase in energy. Since, in the latter case, the temperature of the paste was raised from room temperature to  $30^{\circ}\text{C}$ . only a little while before it was introduced into the cell of the microcalorimeter, it is postulated that heat was required to evaporate dissolved gases so that gas-vapor equilibrium could be re-established at the new temperature. However, more work in this regard needs to be done.

Although very little is known about the effect of hydrogen bonding on thermal conductivity, it has been postulated that an increase in hydrogen bonding should increase this quantity. A higher degree of hydrogen bonding is believed to exist in the water in a clay gel than in a clay sol. Therefore, a miniature thermal probe was used to determine the thermal conductivities of a clay suspension at different times after stirring it (the clay suspensions having more than 4 percent clay by weight gelled on standing). No difference in thermal conductivity was observed with time. Therefore, either no change in the structure of the

water occurred as the gel developed or thermal conductivity is relatively insensitive to changes in water structure.

In order to study the effect of changes in water properties in a clay system on biological activity, a culture of Streptococcus faecalis in TDY broth was introduced, in equal amounts, into two suspensions having the same clay content. One of these suspensions was injected into one cell of the microcalorimeter through an 18-gauge hypodermic needle. The other was stirred and poured into the opposing cell. The former suspension was a gel; the latter was a sol. The two cells were used in a differential arrangement so that the difference in heat produced by the metabolizing microorganisms could be measured. The result was that more heat was produced by the microorganisms in the gel than by those in the sol. However, there was a question about the adsorption of components of the TDY broth on the particle surfaces and the resulting influence this might have on the structure of the adjacent water. Infra-red analysis indicated little or no adsorption. But in order to be safe, it was decided that experiments should be performed to see how much concentration of the broth could be reduced, to minimize adsorption, without reducing the heat production of the organisms below a measurable amount. There was insufficient time to perform these experiments under the present contract. Therefore, the following experiments were conducted instead.

Clay suspensions were introduced into cells of the microcalorimeter by injection through an 18-gauge hypodermic needle and with a spatula.

The latter suspensions had been spun in the viscosimeter prior to their introduction into the calorimetric cells. Therefore, they were more fluid than the former. Then 10 lettuce seeds were placed on the surface of the suspension in each cell. Heats of germination were measured on the individual systems. Also differences in heats of germination were measured by a differential technique. All the results indicated that the germination rate was about 20 percent greater in the gels than in the so-called sols, i.e., the more-fluid suspensions. These results strongly suggest that water properties are different in clay sols than in clay gels and that biological activity is influenced by this difference. However, since some trouble was encountered in aerating the seeds and since more definitive information must be obtained about the state of water in the systems prepared as described, further study of this phenomenon is warranted.

In addition to what has been described heretofore, special heaters, cells, etc., were designed and built for experiments on specific heats, heats of compression and heats of condensation of water in sols and gels. Further, preliminary measurements of specific heats and heats of compression were made. The results were encouraging. However, there was insufficient time to conduct more detailed experiments prior to Dr. Davey's departure.